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TIME-CORRELATION FUNCTIONS
FOR A
ONE-DIMENSIONAL POLYMER MODEL

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Time-Correlation Functions
for a
One-Dimensional Polymer Model

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I INTRODUCTION

Information on the local modes of motion in polymer molecules is of interest because such motion controls rapid relaxation processes.¹ Experimentally these relaxations can be probed in a number of ways, among them dielectric and NMR relaxation and fluorescence depolarization studies. The experimentally determined quantities, such as frequency dependent dielectric susceptibility data, are related to time dependent orientational correlation functions through Fourier transforms. On the fast time-scale, conformational transitions play a major role in the relaxation.

Recently a number of researchers have turned to computer simulations of polymer models as a method of examining the relaxation properties directly.²⁻¹⁰ The models used have varied from full, three-dimensional formulations to simple one-dimensional models with rotational potentials that mimic polymeric systems. Simulation is used on these models to generate representative trajectories, so that the appropriate correlation functions can be calculated.

Another route is to calculate the correlation functions analytically. Because of the complexity of the problem, work in this direction has focused on one-dimensional models such as that pictured in Fig. 1. This model consists of a series of vectors, each situated in a plane perpendicular to a common axis. The vectors are free to rotate in planes orthogonal to the axis, and they interact by way of a nearest neighbor inter-vector pair potential. This model, with a simple one-fold cosine nearest neighbor inter-vector potential, was first studied as a polymer model by Mandell¹¹ using a high temperature power series expansion. Shore and Zwanzig¹² have studied the same model in the low temperature limit by expanding the potential in a power series to quadratic terms and solving the resulting harmonic problem. (The Shore-Zwanzig model has no analogue of conformational transitions.) Mansfield¹³ has completed analytical work on this model with an r -fold cosine potential, drawing upon the coupled spring and dash-pot formulation of Clark and Zimm.¹⁴ The results of these studies have been discussed and compared with Brownian dynamics simulations of the model by Cook and Livornese.³

Recently Hall and Helfand¹⁵ have developed an approach to calculating time dependent correlation functions which, when applied to polymeric systems, focuses upon the rate of passage from one bond state energy minimum to another. In their paper they solve exactly a model containing several of the essential features of models previously studied by Weiner and Pear⁶ and Helfand,^{7,16} viz., a chain of two-state elements. Certain systems with three or more state elements are handled in an approximate way. In the work that follows we will apply techniques similar to that used by Hall and Helfand, and develop a theory for the one-dimensional model in Fig. 1 with an r -fold rotational potential. It is to be emphasized that the theory relates to the time correlation function of the adjacent vector angle differences or "bond states" and not to the individual vector directions. The distinction between these quantities will be discussed later. Comparison will be made with simulation results on the same model to confirm the accuracy of the theory.

The next section reviews the theory with respect to its application to the problem at hand. In section III the simulation results are presented and compared with the theory. The last section offers a discussion of the results.

II. THEORY

Consider a chain of N vectors as described above and pictured in Fig. 1. Let the directions of the vectors be denoted by $\{\phi_i\}$ and their interaction potential by

$$U = \frac{-EkT}{2} \sum_{i=1}^N \cos(r\theta_i) \quad (1)$$

where

$$\theta_i = \phi_{i+1} - \phi_i \quad (2)$$

and E is the barrier to transition, in units of kT , from one potential minimum to another. Note that it is the set of $\{\theta_i\}$ by which the r potential minima are indexed which corresponds to the rotational angle minima defining conformations in a polymer model (especially if $r = 3$). We are interested in understanding the relaxation phenomena of the system due to conformational changes, and thus would like to calculate correlation functions of the type

$$C_i(t) = \langle \cos [\theta_{i+i}(t) - \theta_i(0)] \rangle \quad (3)$$

Let us define the "state" of each θ_j as $\mu_j = 0, 1, \dots, r-1$ depending upon which of the r potential wells (regions between maxima) the θ_j happens to be in. Consider the following allowed transitions at the indicated rates: individual bond conformational transitions

$$\mu_j \rightleftharpoons \mu_j \pm 1, \quad \text{rate } \lambda_0; \quad (4a)$$

counterrotational, cooperative pair transitions, arising as a result of the systems efforts to localize the motion involved in conformational transitions

$$\mu_j \mu_{j+i} \rightleftharpoons (\mu_j \pm 1)(\mu_{j+i} \mp 1), \quad \text{rate } \lambda_i. \quad (4b)$$

Any occurrence of μ_j outside of the range 0 to $r - 1$ is interpreted cyclically, $\mu_j = \mu_j \pm r$. Further assume the chain of N vectors $\{\phi_i\}$ is periodic so that $\theta_j = \theta_{j+N}$. We can denote the full state of the system to be represented by $\mu = (\mu_1, \dots, \mu_N)$. There are r^N states.

We can now represent the correlation function $C_i(t)$ as

$$C_i(t) = \left\langle \cos \left\{ \frac{2\pi}{r} [\mu_{i+i}(t) - \mu_i(0)] + [\alpha_{i+i}(t) - \alpha_i(0)] \right\} \right\rangle \quad (5)$$

where $\theta_i(t)$ has been replaced by $\frac{2\pi}{r}\mu_i(t) + \alpha_i(t)$. $\alpha_i(t)$ is the deviation of $\theta_i(t)$ from the nearest well bottom. Define the correlation function

$$S_i(t) = \left\langle \cos \left[\frac{2\pi}{r} [\mu_{i+i}(t) - \mu_i(0)] \right] \right\rangle. \quad (6)$$

Note that the time for equilibration in a well is short compared to relaxations due to transitions between wells. Therefore we can, to a good approximation, decouple the α and μ states and rewrite Eq. (5) as

$$C_i(t) = S_i(t) \langle \cos [\alpha_{i+i}(t) - \alpha_i(0)] \rangle. \quad (7)$$

The sine terms from the expansion of the cosine of a sum in Eq. (5) have averages equal to zero. The average in Eq. (7) decays rapidly to $\langle \cos \alpha \rangle^2$ and we have

$$C_i(t) = S_i(t) \langle \cos \alpha \rangle^2 \quad (8)$$

where the average is taken over the extent of the well:

$$\langle \cos \alpha \rangle = \int_{-\pi/r}^{+\pi/r} \cos \alpha \exp\left(\frac{E}{2} \cos r \alpha\right) d\alpha \bigg/ \int_{-\pi/r}^{+\pi/r} \exp\left(\frac{E}{2} \cos r \alpha\right) d\alpha. \quad (9)$$

This expression can be easily evaluated numerically, and it is generally close to unity.

It should be emphasized that by reducing the problem from one dealing in the continuous variable set $\{\theta_i\}$ to one of discrete states μ we have limited ourselves to obtaining information on a time scale long compared to the equilibration time in a single well. This is not a serious limitation, however, since the details of short time behavior are handled well by other means, as will be discussed later.

Additionally, we shall see that only the autocorrelation, $C_0(t)$ or $S_0(t)$, are non-zero. This fact can be deduced from the symmetry of the problem, but we will limit ourselves to the explicit demonstration below. The differences between $C_0(t)$ and $S_0(t)$, which occur at short times, will be discussed later.

Let us denote the probability of state μ at time t by $f(\mu, t)$, which may be regarded as an r^N dimensional vector \mathbf{f} with elements $f_\mu(t)$. In this notation the Master Equation can be written as

$$\frac{d\mathbf{f}}{dt} = -\mathbf{M} \mathbf{f}. \quad (10)$$

\mathbf{M} is a $r^N \times r^N$ matrix with elements $M(\mu, \mu') = -\lambda_0$ if μ and μ' differ by the state of a single element j , such that $\mu_j = \mu'_j \pm 1$. There are also elements given by $M(\mu, \mu') = -\lambda_l$ if states μ and μ' differ only by a pair of elements, l apart, such that $\mu_j = \mu'_j \pm 1$ and $\mu_{j+l} = \mu'_{j+l} \mp 1$. More complicated transitions involving three or more elements are neglected. All other off-diagonal terms are zero. The diagonal elements are given by

$$M(\mu, \mu) = - \sum_{\mu' \neq \mu} M(\mu, \mu'). \quad (11)$$

Alternatively \mathbf{M} can be written in operator form as

$$\mathbf{M} = \sum_{j=1}^N \left(\lambda_0 (2 - \mathbf{R}_j^+ - \mathbf{R}_j^-) + \sum_{l=1}^{\infty} \lambda_l (2 - \mathbf{R}_j^+ \mathbf{R}_{j+l}^- - \mathbf{R}_j^- \mathbf{R}_{j+l}^+) \right). \quad (12)$$

Note the index j is to be understood cyclically when outside the range of 1 to N . \mathbf{R}_j^+ and \mathbf{R}_j^- are rotation operators on the μ_j index of a pure state j , raising or lowering it by unity:

$$\mathbf{R}_j^{\pm} | \mu_1, \dots, \mu_j, \dots, \mu_N \rangle = | \mu_1, \dots, \mu_j \pm 1, \dots, \mu_N \rangle. \quad (13)$$

It is convenient to introduce r dimensional vectors referring only to site j , with a set of basis functions $| \mu \rangle_j$. For example, for $r = 3$

$$| 0 \rangle_j = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}_j, \quad | 1 \rangle_j = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}_j, \quad | 2 \rangle_j = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}_j \quad (14)$$

and

$$\mathbf{R}_j^+ \begin{pmatrix} a \\ b \\ c \end{pmatrix}_j = \begin{pmatrix} c \\ a \\ b \end{pmatrix}_j, \quad \mathbf{R}_j^- \begin{pmatrix} a \\ b \\ c \end{pmatrix}_j = \begin{pmatrix} b \\ c \\ a \end{pmatrix}_j. \quad (15)$$

We will call the state

$$|0\rangle_j = \frac{1}{\sqrt{r}} \sum_{\mu} |\mu\rangle_j = \frac{1}{\sqrt{r}} \begin{pmatrix} 1 \\ \vdots \\ 1 \end{pmatrix} \quad (16)$$

the ground state of element j , for reasons which will become clear.

In general, as a complete set of r basis vectors one may also use

$$|\omega\rangle_j = \frac{1}{\sqrt{r}} \sum_{\mu=0}^{r-1} e^{i\omega\mu} |\mu\rangle_j \quad (17)$$

$$\omega = \frac{2\pi p}{r}, \quad p = 0, 1, \dots, r-1. \quad (18)$$

It follows then that

$${}_j\langle\omega' | \omega\rangle_j = \frac{1}{r} \sum_{\mu} \sum_{\mu'} e^{i(\omega\mu - \omega'\mu')} {}_j\langle\mu' | \mu\rangle_j = \delta_{\omega, \omega'}. \quad (19)$$

Additionally the $|\mu\rangle_j$ may be written in terms of $|\omega\rangle_j$ as

$$|\mu\rangle_j = \frac{1}{\sqrt{r}} \sum_{\omega} e^{-i\omega\mu} |\omega\rangle_j. \quad (20)$$

Note that the $|\omega\rangle_j$ are eigenstates of \mathbf{R}_j^{\pm} with eigenvalues $\exp(\mp i\omega)$:

$$\mathbf{R}_j^{\pm} |\omega\rangle_j = \frac{1}{\sqrt{r}} \sum_{\mu} e^{i\omega\mu} |\mu \pm 1\rangle_j = e^{\mp i\omega} |\omega\rangle_j. \quad (21)$$

For example, for $r = 3$ and

$$|\omega\rangle_j = \frac{1}{\sqrt{3}} \begin{pmatrix} 1 \\ e^{i\omega} \\ e^{2i\omega} \end{pmatrix}_j \quad (22)$$

one finds

$$R_j^+ |\omega\rangle_j = \frac{1}{\sqrt{3}} \begin{pmatrix} e^{2i\omega} \\ 1 \\ e^{i\omega} \end{pmatrix}_j = \frac{e^{-i\omega}}{\sqrt{3}} \begin{pmatrix} 1 \\ e^{i\omega} \\ e^{2i\omega} \end{pmatrix}_j = e^{-i\omega} |\omega\rangle_j. \quad (23)$$

Note also that $\omega = 0$ corresponds to the ground state $|0\rangle_j$.

Now consider r^N dimensional basis vectors for developing properties of the whole chain. These can be expressed as the direct product

$$|\omega\rangle \equiv |\omega_1 \omega_2 \dots \omega_N\rangle \equiv |\omega_1\rangle_1 \otimes |\omega_2\rangle_2 \otimes \dots \otimes |\omega_N\rangle_N. \quad (24)$$

We generally only exhibit the non-zero ω 's. For example, a vector with only one non-zero ω , that being at the j th position, is written as $|0 \dots 0 \omega 0 \dots\rangle \equiv |\omega @ j\rangle$. (Note the difference from the r -dimensional vector $|\omega\rangle_j$.) The ground state is $|0\rangle = \frac{1}{r^{N/2}} \begin{pmatrix} 1 \\ \vdots \\ 1 \end{pmatrix}$. Since M is written in terms of the R operators, $|\omega @ j\rangle$ is an eigenstate corresponding to an eigenvalue obtained by substituting $\exp(\mp i\omega)$ for R_j^\pm in M .

In order to calculate correlation functions let us define a function $A_{\nu,j}(\mu)$ such that

$$A_{\nu,j}(\mu) = \delta_{\mu,j,\nu}, \quad (25)$$

i.e., it has value unity when the j th element is in state ν , irrespective of the states of the other elements. $A_{\nu,j}(\mu)$ may be considered a vector $A_{\nu,j}$ labeled with μ :

$$A_{\nu,j} = \sum_{\mu} A_{\nu,j}(\mu) | \mu \rangle. \quad (26)$$

Note that

$$A_{\nu,j} = \begin{pmatrix} 1 \\ \vdots \\ 1 \end{pmatrix} \otimes \begin{pmatrix} 1 \\ \vdots \\ 1 \end{pmatrix} \otimes \dots | \nu \rangle_j \otimes \begin{pmatrix} 1 \\ \vdots \\ 1 \end{pmatrix}. \quad (27)$$

Using Eqs. (16), (20), and (24) we then have

$$A_{\nu,j} = r^{\frac{N-1}{2}} \frac{1}{\sqrt{r}} \sum_{\omega} e^{i\omega\nu} | \omega \otimes j \rangle. \quad (28)$$

Let us calculate

$$\begin{aligned} \langle A_{\nu',j'}(\mu(t)) A_{\nu,j}(\mu(0)) \rangle &= \sum_{\mu} \sum_{\mu'} A_{\nu',j'}(\mu') A_{\nu,j}(\mu) f(\mu', t | \mu) f_{eq}(\mu) \\ &= \sum_{\mu} \sum_{\mu'} A_{\nu',j'}(\mu') A_{\nu,j}(\mu) (\mu' | e^{-Mt} | \mu) \frac{1}{r^N} \\ &= \frac{1}{r^2} \sum_{\omega} \sum_{\omega'} e^{i(\omega\nu - \omega'\nu')} \langle \omega' \otimes j' | e^{-Mt} | \omega \otimes j \rangle \\ &= \frac{\delta_{j,j'}}{r^2} \sum_{\omega \neq 0} e^{i\omega(\nu - \nu')} e^{-m(\omega)t} + \frac{1}{r^2}. \end{aligned} \quad (29)$$

Here $m(\omega)$ is an eigenvalue of M with eigenvector $| \omega \otimes j \rangle$; i.e.

$$\begin{aligned} m(\omega_p) &\equiv \langle \omega \otimes j | M | \omega \otimes j \rangle \\ &= 2\Lambda - \lambda_0(e^{-i\omega} + e^{+i\omega}) - 2 \sum_{l=1}^{\infty} \lambda_l(e^{-i\omega} + e^{+i\omega}) \\ &= 2\Lambda(1 - \cos \omega_p). \end{aligned} \quad (30)$$

The subscript p is added in Eq. (30) to remind us that ω is defined in terms of the integer p in Eq. (18). Λ , the total rate of transitions, is given by

$$\Lambda = \lambda_0 + 2 \sum_{l=1}^{\infty} \lambda_l. \quad (31)$$

In order to evaluate the discrete state correlation function, $S_l(t)$, displayed in Eq. (6), it is necessary to express the quantity to be averaged in terms of the variables $A_{\nu,j}$.

Let us first rewrite Eq. (6) using exponential notation as

$$S_l(t) = \left\langle \exp \left(\frac{2\pi i}{r} (\mu_{j+l}(t) - \mu_j(0)) \right) \right\rangle \quad (32)$$

where we ultimately intend to retain only the real parts. Since $A_{\nu,j}$ is unity if μ_j is in state ν and is zero otherwise, we can express Eq. (32) as

$$\begin{aligned} S_l(t) &= \left\langle \sum_{\nu'=0}^{r-1} A_{\nu',j+l}(t) \exp \left(\frac{2\pi i \nu'}{r} \right) \sum_{\nu=0}^{r-1} A_{\nu,j}(0) \exp \left(\frac{-2\pi i \nu}{r} \right) \right\rangle \\ &= \sum_{\nu'=0}^{r-1} \sum_{\nu=0}^{r-1} \langle A_{\nu',j+l}(t) A_{\nu,j}(0) \rangle \exp \left(\frac{2\pi i (\nu' - \nu)}{r} \right). \end{aligned} \quad (33)$$

Using Eqs. (18) and (29) and rearranging we have

$$\begin{aligned} S_l(t) &= \frac{\delta_{l,0}}{r^2} \sum_{p=1}^{r-1} \exp(-m(\omega_p)t) \left[\sum_{\nu'=0}^{r-1} \sum_{\nu=0}^{r-1} \exp \left(\frac{2\pi i}{r} (\nu - \nu')(p-1) \right) \right] \\ &\quad + \frac{1}{r^2} \sum_{\nu'=0}^{r-1} \sum_{\nu=0}^{r-1} \exp \left(\frac{2\pi i}{r} (\nu' - \nu) \right). \end{aligned} \quad (34)$$

The term in square brackets is non-zero only if $p = 1$ since the r roots of unity sum to zero. Thus, using Eq. (30), we have

$$S_l(t) = \delta_{l,0} \exp \left(-2\Lambda \left(1 - \cos \frac{2\pi}{r} \right) t \right). \quad (35)$$

Note that the theory predicts a single relaxation time regardless of the foldedness of the potential. It can also be shown that higher order autocorrelation functions,

$$S_0^n = \left\langle \cos \left[\frac{2\pi n}{r} [\mu_i(t) - \mu_i(0)] \right] \right\rangle, \quad (36)$$

are given by

$$S_0^n = \exp \left(-2\Lambda \left(1 - \cos \frac{2\pi n}{r} \right) t \right). \quad (37)$$

III. SIMULATIONS

In order to check the theory, Brownian dynamics simulations were performed on the model. The method of Brownian dynamics simulation applied to this model has been described previously³ and will be briefly reviewed here.

The set of equations to be solved has the form

$$\frac{d^2\phi_i}{dt^2} = -\frac{\partial U}{\partial \phi_i} - \eta \frac{d\phi_i}{dt} + L_i(t) \quad (38)$$

where η is the coefficient of friction associated with the motion of the vector through the solvent and $L_i(t)$ represents the randomly fluctuating force of the solvent on individual vectors. $L_i(t)$ is assumed to be Gaussian with first and second moments given by

$$\langle L_i(t) \rangle = 0 \quad (39)$$

$$\langle L_i(t_1) L_j(t_2) \rangle = 2kT\eta\delta_{ij}\delta(t_1 - t_2) \quad (40)$$

In the highly viscous limit where the time steps used, Δt , are much larger than the velocity relaxation times, the acceleration term may be dropped and Eq. (38) rewritten to first order in Δt in a form suitable for computer simulation as

$$\phi_i(t + \Delta t) = \phi_i(t) - \frac{1}{\eta} \frac{\partial U}{\partial \phi_i} \Delta t + \frac{1}{\eta} B_i(\Delta t) \quad (41)$$

where

$$B_i(\Delta t) = \int_0^{\Delta t} L_i(t + s) ds. \quad (42)$$

$B_i(\Delta t)$ is characterized by a Gaussian probability such that¹⁷

$$P(B_i(\Delta t)) = (4\pi\eta kT\Delta t)^{-\frac{1}{2}} \exp\left(\frac{-[B_i(\Delta t)]^2}{4\eta kT\Delta t}\right) \quad (43)$$

We scale the friction coefficient together with the time step by defining a reduced time

$$t' = \left(\frac{kT}{\eta} \right) t \quad (44)$$

so that Eq. (41) becomes

$$\phi_i(t' + \Delta t') = \phi_i(t') - \frac{1}{kT} \frac{\partial U}{\partial \phi_i} \Delta t' + \sqrt{2\Delta t'} b_i. \quad (45)$$

$B_i(\Delta t)$ is replaced by the scaled b_i , whose values are governed by a Gaussian distribution with variance equal to one. The simulations were based on Eq. (45) for systems of 100 vectors with periodic boundary conditions, and a time step $\Delta t'$ of .001. For simplicity we have dropped the prime notation on t in what follows.

The time dependent autocorrelation shown in Eq. (3) was calculated for a $5kT$ barrier with both a 3-fold and 5-fold cosine potential and also for an $8kT$ barrier with the 3-fold potential. Since the theory focuses on states $\{\mu\}$ rather than the continuous variable $\{\theta\}$ we have also calculated $S_0(t)$ as displayed in Eq. (6) for the 3-fold $5kT$ system to show that it is in fact proportional to $C_0(t)$ at all but short times. Operationally, $\mu_j(t)$ is defined to change value only when the θ_j passes through the potential minimum of an adjacent well. Thus it is possible for a θ_j to move from one potential minimum over a barrier, part way down to the next minimum and back again without changing the value of $\mu_j(t)$. This definition is consistent with that used in the hazard analyses that will follow and is based upon earlier work by Helfand^{7,9} on systems with similar characteristics. At times greater than the minimum transition

time, $S_0(t)$ and $C_0(t)$ relax with the same time constant as shown in Fig. 2 for the 3-fold $5kT$ system. Note the differences at short times where the initial decay of $C_0(t)$ goes as $\exp(-t)$,¹² but shifts over rapidly to $\exp(-t/\tau)$ where τ is the characteristic conformational relaxation time. The ratio of $C_0(t)$ to $S_0(t)$ is $\langle \cos \alpha \rangle^2$. For the 3-fold $5kT$ system the ratio varies from 0.95 to 0.94 for times greater than about 0.5 time units. This compares favorably with a value of 0.94 calculated from Eq. (9).

To apply the theory we need to know the value of Λ in Eq. (35). As will be shown later, for these systems Λ is only slightly larger than λ_0 , the cooperative transitions having much lower rates. If we treat the potential as quadratic with curvature $\gamma = \frac{1}{2}r^2E$ in the wells and at the barriers, Kramers' theory¹⁸ as developed by Helfand^{7,18} for polymeric systems gives for $\eta = 1$

$$\lambda_0 = \frac{4}{3} \frac{\gamma}{2\pi} e^{-E}, \quad (46)$$

which is 4/3 times the simple Kramers expression for the single isolated barrier problem. The factor of 4/3 is due to the frictional resistance of the chain tails.¹⁹ A more exact expression for the multi-welled cosine potential of Eq. (1) has been developed in the Appendix and gives for unit viscosity

$$\lambda_0 = \left(\frac{4}{3}\right) \left(\frac{r}{2\pi I_0(E/2)}\right)^2 \quad (47)$$

where $I_0(E/2)$ is a zeroth order modified Bessel function. The use of the 4/3 factor in this expression may not be rigorous since the factor was originally developed for a

system with quadratic potentials. However the excellent agreement of Eq. (47) with the simulation results discussed below is encouraging.

The value of Λ can also be estimated directly from the simulations by use of hazard analysis as developed for polymer systems by Helfand.^{7,9} Basically one orders the times for n transitions, from one well minimum to another, that take place during the simulation. Then one plots the expectation value of the cumulative hazard for the k th ordered transition,

$$H_k = \sum_{l=0}^{k-1} \frac{1}{n-l} \quad (48)$$

against the transition time of the k th ordered transition. The rate of transition is the asymptotic slope of this plot divided by two, since each transition from a well can occur in two directions. Since the rate obtained considers all transitions including those that are part of a coupled transition we are measuring Λ rather than λ_0 . The differences are small however. Figure 3 shows the hazard plot for the 3-fold $5kT$ simulation. The inset shows that the plot does not intersect the origin, due to the initial transition time, t_t , necessary for a movement from one well minimum to another. The first three columns of Table I present rate values obtained from: the simple Kramers formula, Eq. (46); from our revised formula, Eq. (47); and Λ from the hazard analyses for systems with $5kT$ barriers. Note the excellent agreement of our revised λ_0^{rK} with the hazard results.

Figure 4 shows plots of $\ln C_0(t)$ against t for the systems studied. Note the linearity indicating a single relaxation time. The slopes of these lines are simply the coefficients

of t in Eq. (35). Thus the characteristic relaxation time τ is

$$\tau = \left[2\Lambda \left(1 - \cos \frac{2\pi}{r} \right) \right]^{-1}. \quad (49)$$

The last three columns of Table I show: first τ^{rK} which uses λ_0^{rK} calculated by the revised Kramers' formula to approximate Λ ; then τ^h which is based upon the Λ extracted from the hazard plots; and finally τ^c which was determined directly from the correlation functions, $C_0(t)$, obtained from the simulations. Agreement between the simulation and theoretical results is in general good. The differences will be discussed in the next section.

The hazard plots also give us an opportunity to estimate the fraction of correlated transitions which occur. These can be of two types. First there is the possibility that a bond, having made a transition, will find the environment unfavorable and immediately move back. This is reflected in a somewhat enhanced slope in the hazard plot at short times shown in Fig. 3. Helfand⁷ has shown that the fraction of back reactions, c_0 , is given by $c_0 = 1 - \exp(-H_I^0)$. H_I^0 is the value of the asymptotic linear portion (dashed in Fig. 3) of the hazard data at t_t , the minimum transition time from well to well. The values of c_0 are listed in Table II for the $5kT$ barrier systems.

In order to probe correlated transitions between neighboring bond states we need to make hazard plots associated with neighbor transitions. The procedure is the same except that the ordered times are the times for neighboring bonds to undergo a transition measured from a zero of time based on the central bonds transition. As

described by Helfand⁷ these plots are also linear except at short times as shown in Fig. 5. Only relatively short time data is shown for first(1), second(2), and third(3) neighbor transitions. The linear portions of these plots have slopes twice that of the "auto" hazard plots since each bond has two neighbors. The fraction of correlated transitions is given in a manner analogous to that for back reactions, namely $c_l = 1 - \exp(-H_l^t)$, where H_l^t is evaluated at $t = 0$. The results for the 3- and 5-fold systems with a barrier of $5kT$ are shown in Table II.

IV. DISCUSSION

Agreement of the relaxation times calculated only by theory(τ^K) or by theory and Λ from hazard analyses (τ^h) with those directly from the simulations (τ^c) is excellent. The simulations give a somewhat longer relaxation time due partly to the fact that the Λ obtained from the hazard analysis counts as two transitions (one short time, the other long) situations in which a vector pair, having made a transition, finds itself in an unfavorable environment and reverses itself immediately. These paired transitions, representing about 3 per cent(or c_0) of the transitions, clearly do not contribute to the long time relaxation of the system. This, coupled with the few percent uncertainty in the values of Λ from the hazard analysis and τ^c from the simulations show the theory to be consistent with the simulation results.

Though of interest by itself, the correlation function $C^\theta(t)$ of Eq. (3) does not relate to the usual experimentally observable quantities, since the θ 's are rotational bond angles. The relaxation of the ϕ 's however, if interpreted as dipole vectors, can be related to the frequency dependent dielectric response through the Fourier transform of the derivative of the correlation function $C^\phi(t)$ where²⁰

$$C^\phi(t) = \langle \cos [\phi_i(t) - \phi_i(0)] \rangle. \quad (50)$$

Investigations of $C^\phi(t)$ for this model have been recently presented by Cook and Livornese³. Unfortunately no rigorous mathematical relationship giving $C^\phi(t)$ in terms of $C^\theta(t)$ is evident. Additionally $C^\phi(t)$ involves a relaxation equivalent to a polymer

tumbling mode not present for $C^\theta(t)$ which involves only internal coordinates. Single relaxation time decay, observed for $C^\theta(t)$, seem to be valid also for $C^\phi(t)$ at times longer than about 0.5 time units, and is probably related to the transition rate from well to well. For the 3-fold $5kT$ system the time constant τ is about twice as large for $C^\theta(t)$ as for $C^\phi(t)$.

As noted earlier, the present theoretical calculation cannot give the short time behavior since it ignores the continuous nature of the θ variable. The relaxations which occur in the well before transition can probably be accurately described by a quadratic expansion of the potential along the lines of Shore and Zwanzig¹². At very short times where $\Delta t \ll \sqrt{\Delta t}$, $C^\theta(t)$ as well as $C^\phi(t)$ are governed only by the random force and thus go as $\exp(-t)$.

As a final note let us mention two important differences between the one-dimensional model studied here and three-dimensional systems, both as model simulations and real physical systems. First we noted that for our one-dimensional system coupled transitions were of relatively little importance. In three-dimensional models Helfand, et al.,⁹ have shown that correlated transitions with second neighbor bonds are quite important for understanding the local motions. Second, we note that the simple exponential relaxation observed for this one-dimensional model with symmetric rotational possibilities is not observed experimentally for real polymer systems. Significant non-exponential behavior as measured, for example, by non-semicircular Cole-Cole

plots, is the rule rather than the exception. Viovy, Monnerie, and Brochon²¹ must invoke more than an exponential function to fit their fluorescence depolarization studies, as must Connolly, Gordon and Jones²² for their NMR data. Contrasting the present model with that of Hall and Helfand¹⁵ we see that such differences can arise from the presence of the cis barrier. Under glassy conditions totally different mechanisms probably have to be invoked.

ACKNOWLEDGMENT

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APPENDIX

For an arbitrary potential U with wells at points A and B separated by a barrier at point C , Kramers¹⁸ has shown that in the case of high viscosity the rate of passage of particles(in our case bond states) from A to B over the barrier at C is

$$\Gamma = \frac{w}{n_A}, \quad (A1)$$

where w is the diffusion current given by

$$w = \frac{kT\sigma_A}{\eta} \left(\int_A^B e^{U/kT} dq \right)^{-1}, \quad (A2)$$

n_A is the number of bond states near A , and σ_A is the bond density near A . For convenience we pick well A at $\theta = 0$ so that

$$n_A = \sigma_A \int_{-\pi/r}^{\pi/r} \exp\left(\frac{E}{2} \cos r\theta\right) d\theta = \frac{2\pi\sigma_A I_0(E/2)}{r} \quad (A3)$$

where $I_0(E/2)$ is a zeroth order modified Bessel function.²³ Substituting the potential in Eq. (1) into Eq. (A2) gives

$$w = \frac{kT\sigma_A}{\eta} \left(\int_0^{2\pi/r} \exp\left(-\frac{E}{2} \cos r\theta\right) d\theta \right)^{-1} = \frac{kT\sigma_A r}{2\pi\eta I_0(E/2)}. \quad (A4)$$

The rate of passage Γ is thus given by

$$\Gamma = \frac{kT}{\eta} \left(\frac{r}{2\pi I_0(E/2)} \right)^2. \quad (A5)$$

For a single isolated barrier, in the units of the problem at hand,

$$\lambda_0 = \left(\frac{r}{2\pi I_0(E/2)} \right)^2. \quad (A6)$$

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Table I. The values of the rates λ_0^{eK} , obtained from Eq. (40); λ_0^{rK} , obtained from Eq. (41); Λ^h , obtained from the hazard data; along with relaxation times τ^{rK} and τ^h , obtained from λ_0^{rK} and Λ^h by use of Eq. (43); and τ^c measured directly from the simulations are presented for the systems studied.

system	λ_0^{eK}	λ_0^{rK}	Λ^h	τ^{rK}	τ^h	τ^c
3-fold $5kT$	0.0322	0.0281	0.0277	11.87	12.03	12.27
5-fold $5kT$	0.0894	0.0780	0.0787	9.28	9.19	9.72
3-fold $8kT$	0.0016	0.0024	-	140.1	-	154.

Table II. Values of c_l , the fraction of transitions that represent either back-reactions, $l = 0$, or coupled transitions, $l = 1, 2, 3$, with the first, second or third neighbor.

system	c_0	c_1	c_2	c_3
3-fold $5kT$	0.030	0.16	0.06	0.03
5-fold $5kT$	0.024	0.16	0.06	0.03

Figure Captions

Figure 1. Schematic representation of the one-dimensional model. Each vector can rotate in a plane perpendicular to a common axis. Its degree of rotation, ϕ , is measured relative to an arbitrary external direction.

Figure 2. $C_0(t)$ and $S_0(t)$ simulation results for the three-fold system with barrier heights of $5kT$. Note that only at very short times do the relaxation rates of the two correlation functions differ.

Figure 3. A hazard plot of times between transitions of the same bond state. The expectation value of the k th cumulative hazard is plotted against the k th smallest transition time. The inset shows a slightly enhanced transition rate at short times which follows a short time gap, t_t , corresponding to the minimum time necessary for a transition. The intercept indicated by the dotted line is a measure of the fraction of rapid back reactions.

Figure 4. Logarithm of $C_0(t)$ is plotted against time for the three systems studied. The relaxation time τ is equal to the negative of the inverse slope, and is nearly constant for times greater than about 0.2 time units.

Figure 5. A hazard plot of times between transitions of neighboring bond states where the expectation value of the k th cumulative hazard is plotted against the k th ordered transition time. Plots for first(1), second(2), and third(3) neighbor transitions

are shown. The enhanced slope at short times is due to coupled transitions. Only data for relatively short time transitions is shown(compare with Fig. 3).

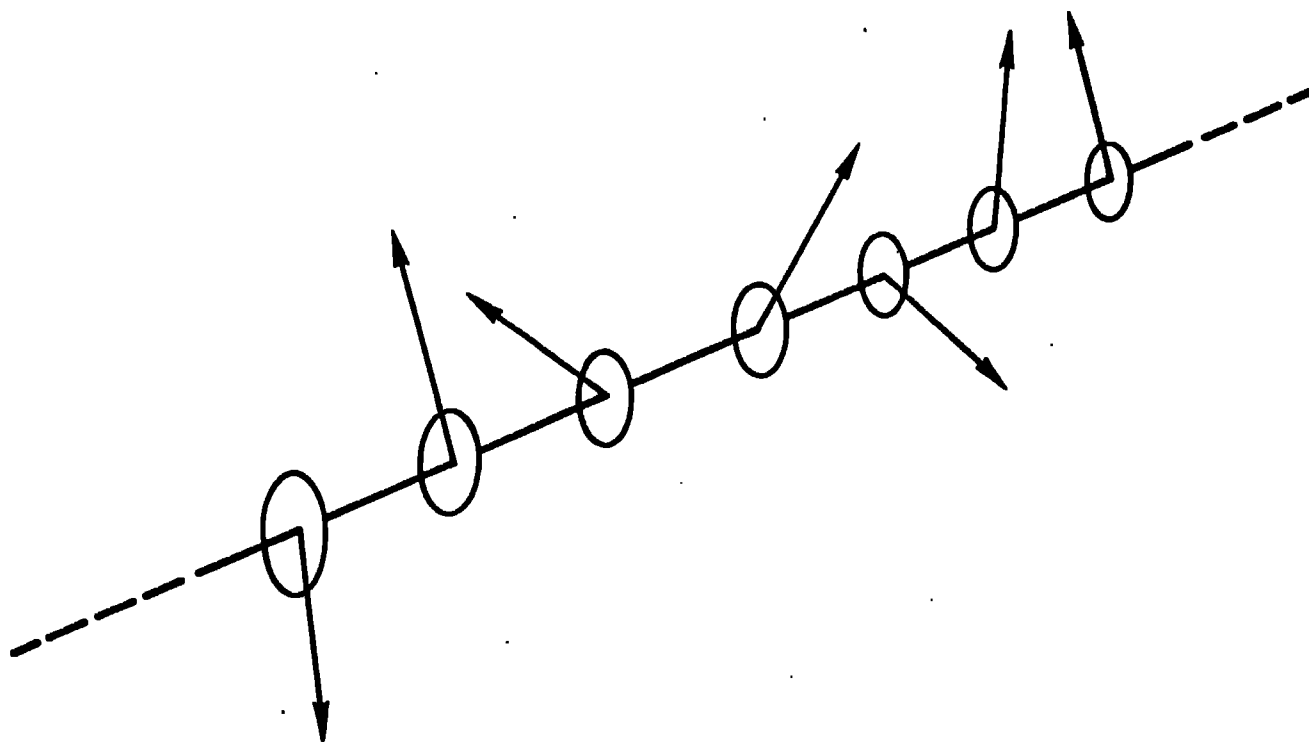


FIGURE 1.

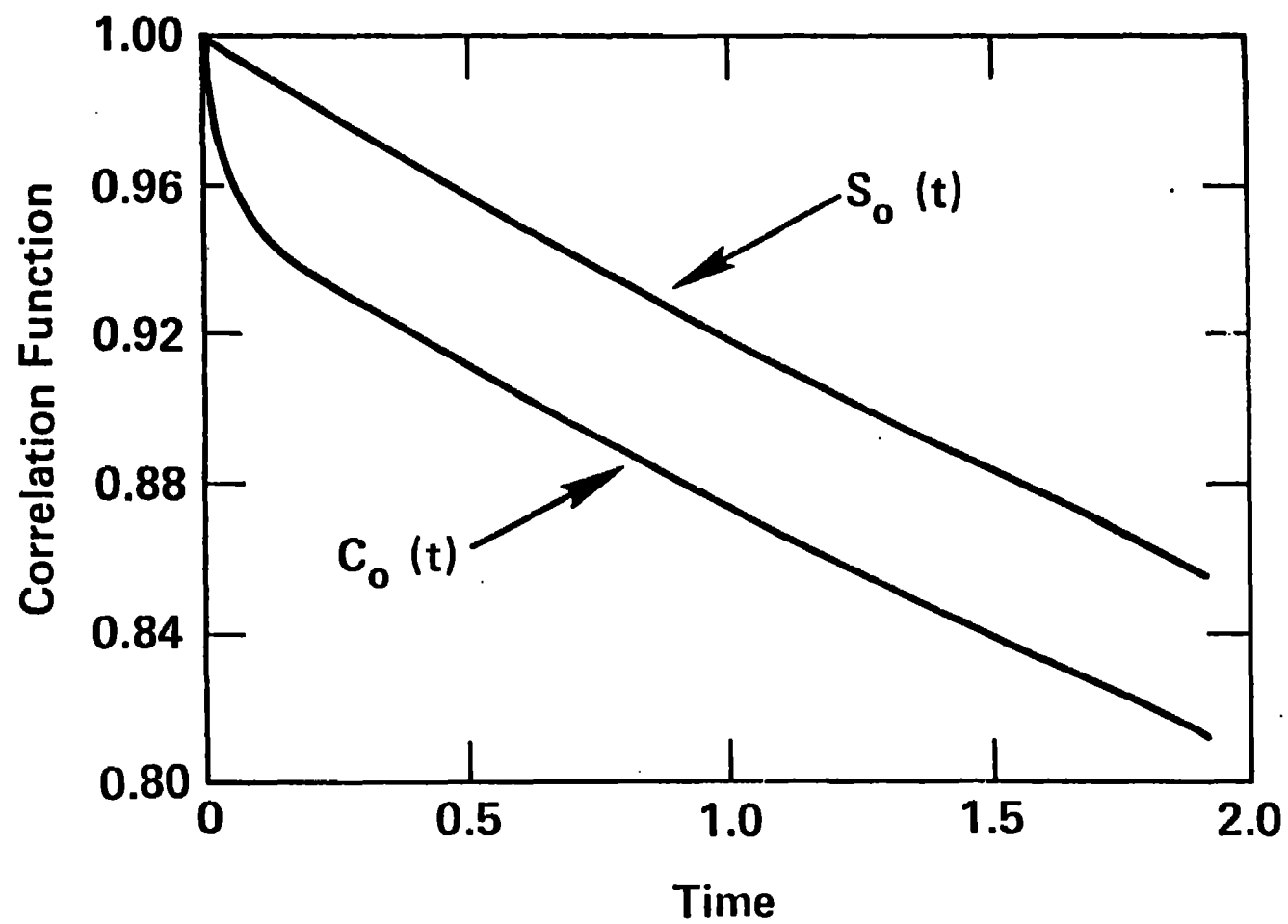


FIGURE 2 .

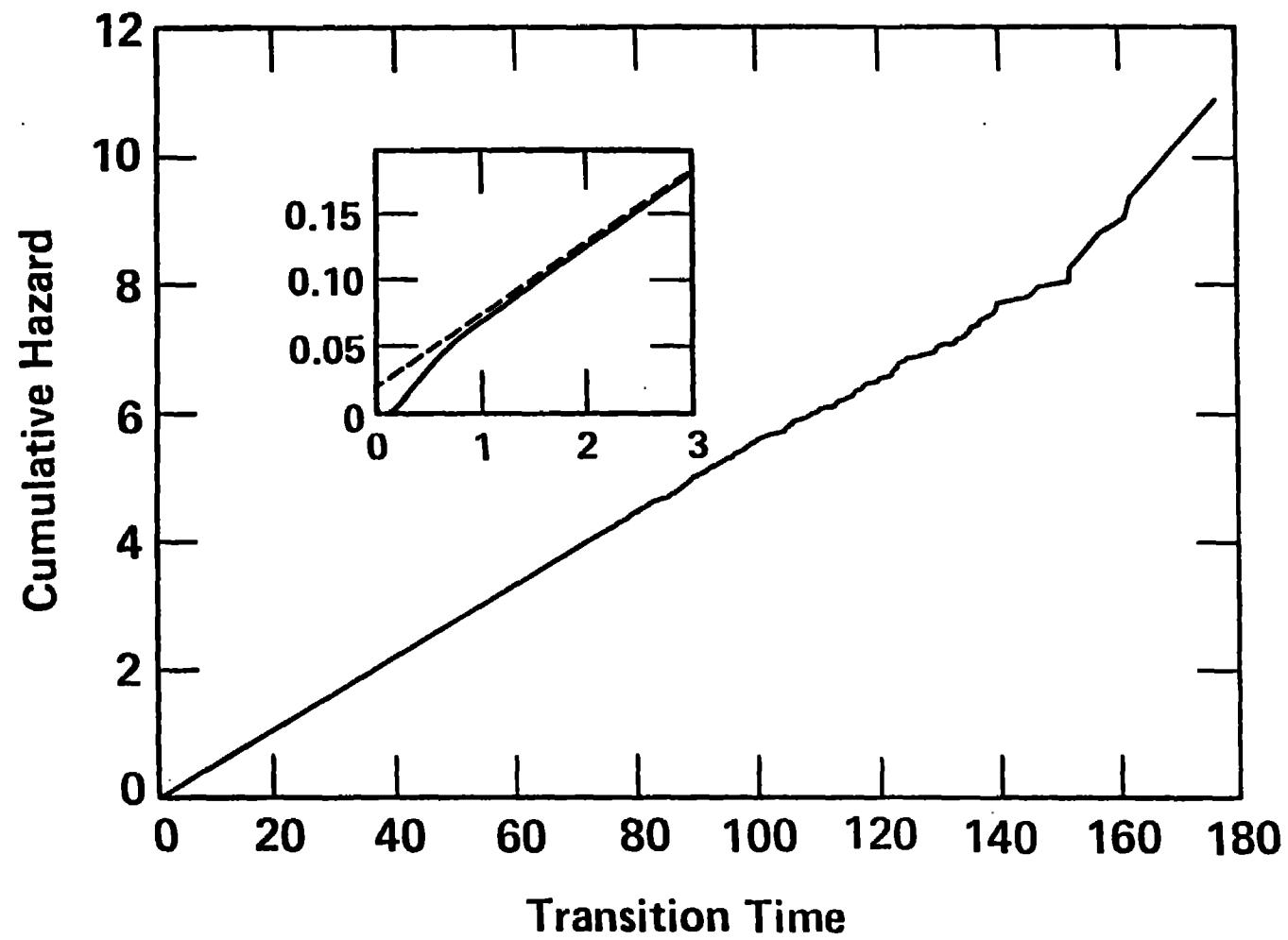


FIGURE 3.

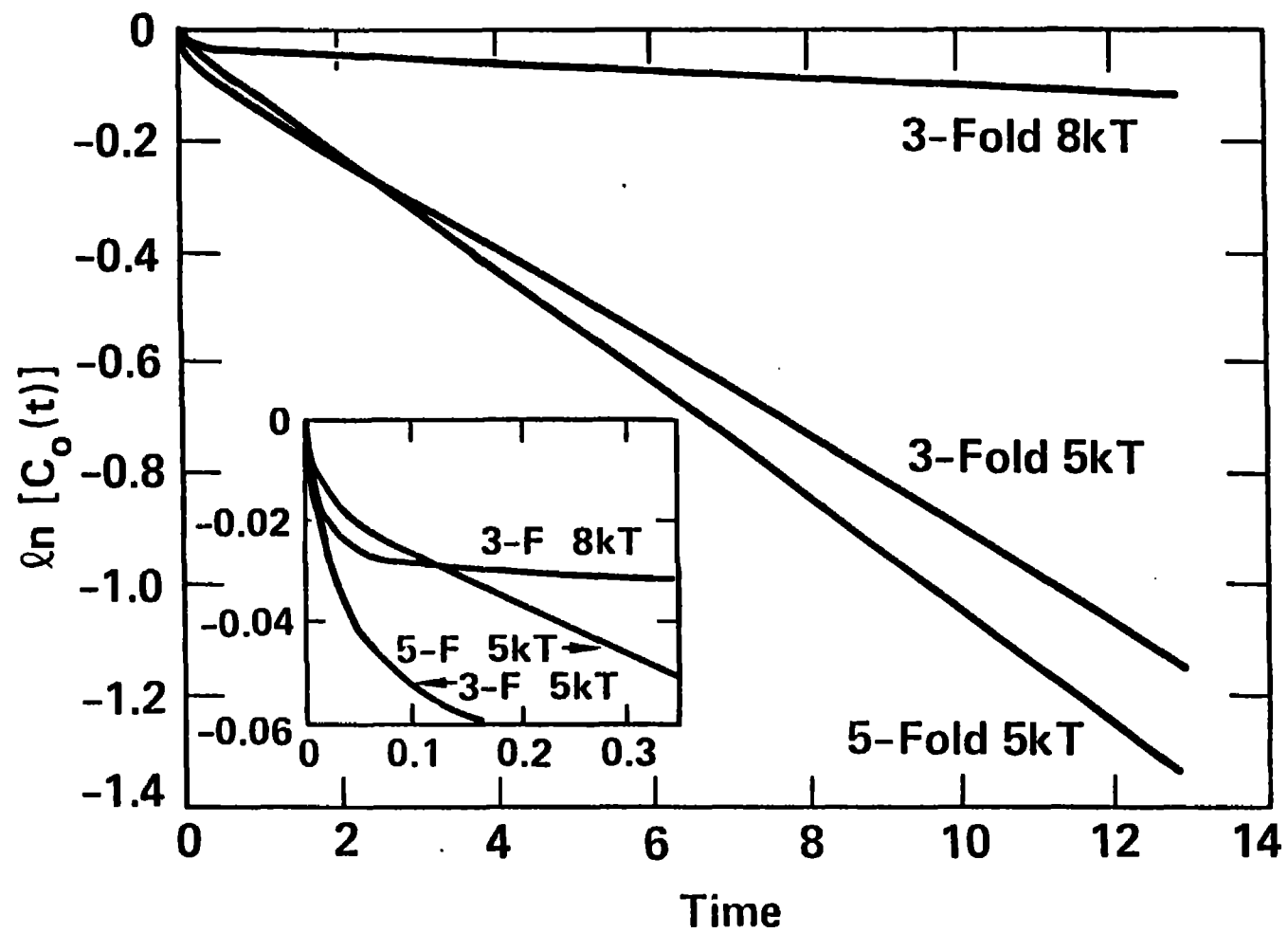


FIGURE 4.

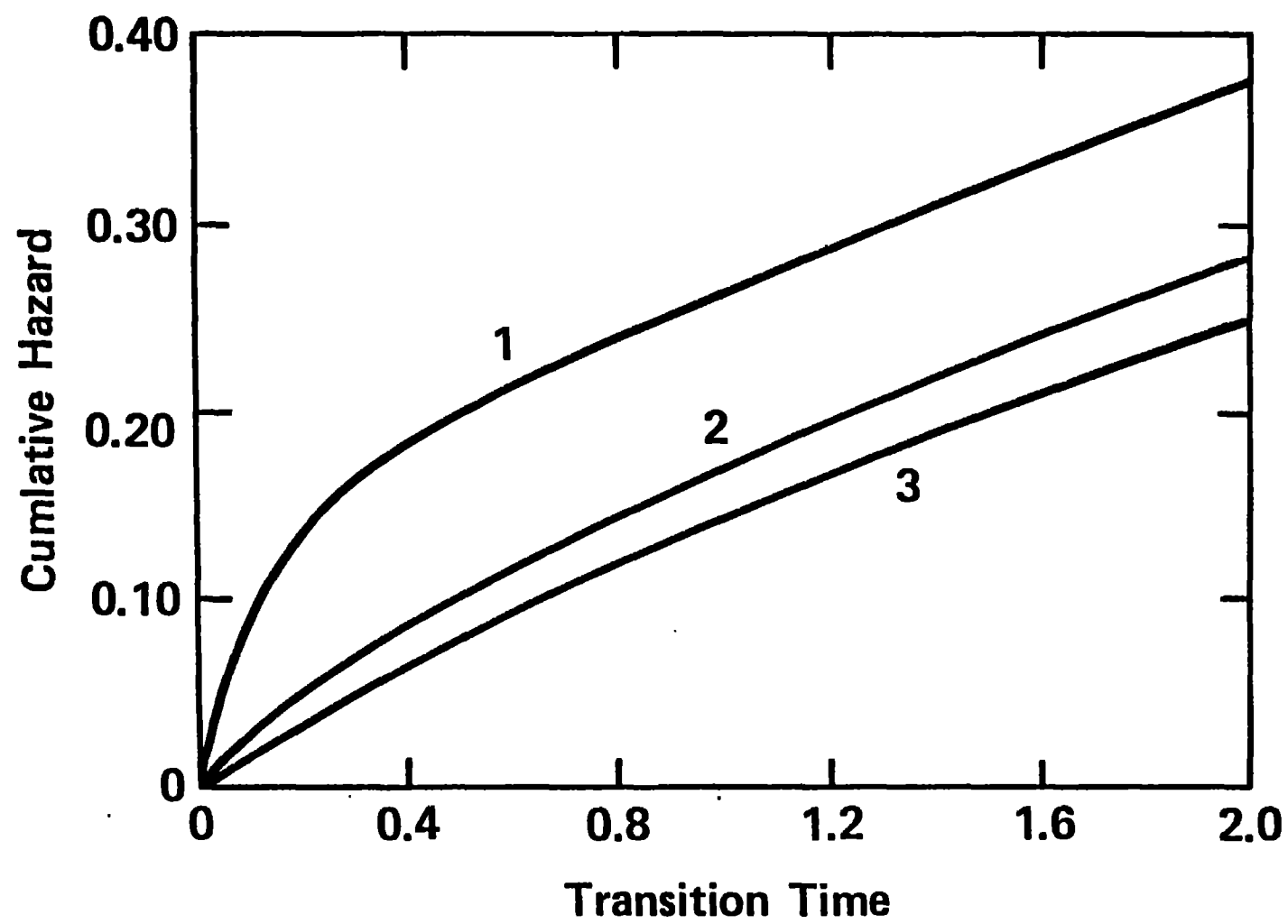


FIGURE 5.